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CLAIMS

- 1. An aqueous acidic immersion plating solution having a pH of from about 3.5 to about 6.5 comprising zinc ions, nickel and/or cobalt ions, and fluoride ions provided that the solution is free of cyanide ions.
- 2. The immersion plating solution of claim 1 also containing at least one inhibitor containing one or more nitrogen atoms, one or more sulfur atoms, or both sulfur and nitrogen atoms.
- 3. The immersion plating solution of claim 1 also containing one or more metal complexing agents.
- 4. The immersion plating solution of claim 1 also containing one or more additional metal ions selected from copper ions, iron ions, manganese ions, magnesium ions and zirconium ions.
- 5. The immersion plating solution of claim 2 wherein the inhibitor is selected from nitrogen-containing disulfides; alkali metal thiocyanates; thiocarbamates; nitrogen-containing heterocyclic compounds; mercapto substituted nitrogen-containing heterocyclic compounds, thioacids, thioalcohols, compounds characterized by the formula

 $R_2N-C(S)Y$

wherein each R is independently hydrogen or an alkyl, alkenyl, or aryl group, and Y is $X R^1$, NR_2 or $N(H)NR_2$; wherein X is O or S and R^1 is hydrogen or an alkali metal; and mixtures thereof.

6. The immersion plating solution of claim 2 wherein the inhibitor is a thiourea compound represented by the formula:

 $[R_2N]_2CS$

wherein each R is independently hydrogen or an alkyl, alkenyl or aryl group.

- 7. The immersion plating solution of claim 2 wherein the inhibitor is at least one nitrogen containing heterocyclic compound or mercapto substituted nitrogen containing heterocyclic compound, or mixtures thereof.
- 8. The immersion plating solution of claim 7 wherein the heterocyclic compound is selected from pyrroles, imidazoles, benzimidazoles, pyrazoles, triazoles, pyridines, piperazines, pyrazines, piperidines, pyrimidines, thiazoles, thiazolines, thiazolidines, rhodamines, and morpholines.
- 9. The immersion plating solution of claim 2 wherein the inhibitor is a mercapto substituted nitrogen containing heterocyclic compound.
 - 10. The immersion plating solution of claim 1 containing:

 from about 1 to about 150 g/l of zinc ions, and

 from about 5 to about 250 g/l of nickel and/or cobalt ions.
- 11. The immersion plating solution of claim 10 wherein the solution also contains from about 0.0005 to about 5 g/l of an inhibitor containing one or more nitrogen atoms, one or more sulfur atoms, or both sulfur and nitrogen atoms.
- 12. The immersion plating solution of claim 1 which is free of aliphatic amines and aliphatic hydroxylamines.
- 13. An aqueous acidic immersion plating solution having a pH of from about 3.5 to about 6.5 and comprising:

from about 1 to about 150 g/l of zinc ions,
from about 5 to about 250 g/l of nickel and/or cobalt ions, and
from about 0.005 to about 100 g/l of fluoride ions
provided the solution is free of cyanide ions.

- 14. The immersion plating solution of claim 13 also containing: from about 0.005 to about 100 g/l of an inhibitor containing one or more nitrogen atoms, one or more sulfur atoms, or both sulfur and nitrogen atoms.
- 15. The immersion plating solution of claim 13 also containing at least one metal complexing agent.

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- 16. The immersion plating solution of claim 15 wherein the metal complexing agent is selected from an acetate, citrate, glycollate, lactate, maleate, pyrophosphate, tartrate, gluconate, or glucoheptonate, and mixtures thereof.
- 17. The immersion plating solution of claim 14 wherein the inhibitor is selected from nitrogen-containing disulfides, alkali metal thiocarbamates, nitrogen-containing heterocyclic compounds, mercapto substituted nitrogen-containing heterocyclic compounds, thioacids, thioalcohols, compounds characterized by the formula

 $R_2N-C(S)Y$

wherein each R is independently hydrogen or an alkyl, alkenyl, or aryl group, and Y is XR¹, NR₂ or N(H)NR₂, wherein X is O or S and R¹ is hydrogen or an alkali metal and mixtures thereof.

18. The immersion plating solution of claim 14 wherein the inhibitor is a thiourea compound represented by the formula:

[R₂N]₂CS II

wherein each R is independently hydrogen or an alkyl, alkenyl or aryl group.

- 19. The immersion plating solution of claim 14 wherein the inhibitor is at least one nitrogen containing heterocyclic compound or a mercapto substituted nitrogen containing heterocyclic compound or mixtures thereof.
- 20. The immersion plating solution of claim 19 wherein the heterocyclic compound is selected from pyrroles, imidazoles, pyrazoles, triazoles, tetrazoles, thiazoles, thiazolines, thiazolidines, pyridines, piperazines, pyrazines, piperidines, pyrimidines, and morpholines.
- 21. The immersion plating solution of claim 14 wherein the inhibitor is a mercapto substituted nitrogen containing heterocyclic compound.

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- 22. The immersion plating solution of claim 13 having a pH of from about 4 to about 6.
- 23. The immersion plating solution of claim 13 also containing one or more metal ions selected from copper ions, iron ions, manganese ions, magnesium ions and zirconium ions.

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- 24. The immersion plating solution of claim 13 which is free of aliphatic amines and aliphatic hydroxylamines.
- 25. A non-cyanide aqueous acidic immersion plating solution having a pH of from about 4 to about 6 and comprising:

from about 10 to about 30 g/l of zinc ions,
from about 20 to about 50 g/l of nickel and/or cobalt ions,
from about 0.5 to about 10 g/l of fluoride ions, and
from about 0.005 to about 0.05 g/l of an inhibitor containing one
or more nitrogen atoms, one or more sulfur atoms, or both sulfur and nitrogen
atoms.

- 26. The immersion plating solution of claim 25 also containing:

 from about 1 to about 250 g/l of at least one metal complexing agent.
- 27. The immersion plating solution of claim 25 wherein the inhibitor is a mercapto substituted nitrogen containing heterocyclic compound.
- 28. A process for depositing a zinc alloy protective coating on aluminum or aluminum based alloy substrates which comprises
- (A) immersing an aluminum or aluminum based alloy substrate in an aqueous acidic immersion plating solution of claim 1 for a period of time sufficient to deposit the desired coating, and
- (B) removing the coated substrate from the immersion plating solution.
- 29. The process of claim 28 wherein the surface of the aluminum or aluminum based alloy is cleaned, etched and desmutted prior to immersion in the immersion plating solution.

- 30. The process of claim 29 wherein the cleaning is performed with an alkaline, acidic, or solvent cleaner, and the etching is performed with an alkaline or acid etching solution.
- 31. The process of claim 29 wherein the aluminum or aluminum based alloy is rinsed with water after each of the cleaning, etching, desmutting, and immersion plating steps.

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- 32. A process for depositing a zinc alloy protective coating on aluminum or aluminum based alloy substrate which comprises
- (A) immersing the substrate in an aqueous acidic immersion plating solution of claim 13 for a period of time sufficient to deposit the desired coating, and
- (B) removing the coated substrate from the immersion plating solution.
- 33. The process of claim 32 wherein the surface of the substrate is cleaned, etched and desmutted prior to immersion in the immersion plating solution.
- 34. The process of claim 33 wherein the cleaning is performed with an alkaline, acidic or solvent cleaner, and the etching is performed with an alkaline or acid etching solution.
- 35. The process of claim 34 wherein the substrate is rinsed with water after each of the cleaning, etching, desmutting, and immersion plating steps.
- 36. A process for depositing a zinc alloy protective coating on aluminum or aluminum based alloy substrate which comprises
- (A) immersing the substrate in an aqueous acidic immersion plating solution of claim 25 for a period of time sufficient to deposit the desired coating, and
- (B) removing the coated substrate from the immersion plating solution.
- 37. The process of claim 36 wherein the surface of the substrate is cleaned, etched and desmutted prior to immersion in the immersion plating solution.
- 38. The process of claim 37 wherein the cleaning is performed with an alkaline, acidic, or solvent cleaner, and the etching is performed with alkaline or acid etching solution.

- 39. The process of claim 37 wherein the substrate is rinsed with water after each of the cleaning, etching, desmutting, immersion plating steps.
- 40. A process for depositing a metal coating on an aluminum or aluminum alloy substrate comprising
- (A) applying an immersion zinc alloy protective coating on the substrate by immersing the substrate in an aqueous acidic immersion plating solution of claim 1, and
- (B) plating the zinc alloy coated substrate using an electroless or electrolytic metal plating solution.
- 41. The process of claim 40 wherein the surface of the substrate is subjected to cleaning, acid etching and desmutting, prior to immersion in the immersion plating solution.
- 42. The process of claim 41 wherein the cleaning is performed with an alkaline, acidic, or solvent cleaner, and the etching is performed with alkaline or acid etching solution.
- 43. A process for depositing a metal coating on an aluminum or aluminum alloy substrate comprising
- (A) applying an immersion zinc alloy protective coating on the substrate by immersing the substrate in an aqueous acidic immersion plating solution of claim 13, and
- (B) plating the zinc alloy coated substrate using an electroless or electrolytic metal plating solution.
- 44. The process of claim 43 wherein the surface of the substrate is subjected to alkaline, acidic or solvent cleaning, acid etching and desmutting, prior to immersion in the immersion plating solution.
- 45. The process of claim 44 wherein the cleaning is performed with an alkaline cleaner, and the etching is performed with alkaline or acid etching solution.
- 46. A metal coated aluminum or aluminum based alloy obtained in accordance with the process of claim 40.

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- 47. A metal coated aluminum or aluminum based alloy obtained in accordance with the process of claim 43.
- 48. A metal coated aluminum or aluminum based alloy obtained in accordance with the process of claim 44.
- 49. A metal coated aluminum or aluminum based alloy obtained in accordance with the process of claim 45.